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COMPLETE SPECIFICATION

Catalytic Conversion of Ethane to Vinyl Chloride

We, PRINCETON CHEMICAL RESEARCH INC., a Corporation organised and existing under the laws of the State of New Jersey, United States of America, of P.O. Box 652, Princeton, State of New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to the catalytic conversion of ethane to vinyl chloride.

Vinyl chloride may be produced by a catalytic reaction involving acetylene and hydrogen chloride, or by the pyrolyzation of ethylene dichloride which, in turn, may be produced by reaction of ethylene and chlorine.

It has also been proposed to produce vinyl chloride by the oxychlorination of ethane with the use of a Deacon-type catalyst, and notably a copper chloride catalyst deposited on a support. These catalysts, however, generally have but a limited life at the required reaction temperatures and the yield of vinyl chloride under the reaction conditions taught is relatively low.

It has furthermore been proposed to dehydrogenate saturated hydrocarbons or chlorinated saturated hydrocarbons using various types of dehydrogenating catalysts and small quantities of hydrogen chloride, and the chlorination of unsaturated hydrocarbons, such as olefins, is, of course, known.

The reaction conditions which favour the dehydrogenation, however, generally do not favour the chlorination and *vice versa*. Furthermore, a chlorination reaction generally proceeds with the formation of substantial quantities of polychlorinated products.

An object of this invention is an improved catalytic process for the conversion of ethane with a high yield of vinyl chloride.

We have discovered that ethane may be effectively converted to vinyl chloride in a

catalytic oxidation reaction if steam, available chlorine and oxygen are used in specific controlled ratios.

This invention provides a process for the catalytic conversion of ethane to vinyl chloride which comprises reacting a mixture of ethane, available chlorine and oxygen at a temperature between 500 and 750°C. (preferably between 500 and 675°C.) in the presence of added water and an oxidation catalyst, said available chlorine being added in amount of at least one gram atom per mole of ethane and per mole of oxygen, and said water being added in amount of at least 2 moles per mole of ethane.

The chlorine is usually added in the form of hydrogen chloride. However, the chlorine can be introduced to the reaction zone as, for example, Cl_2 or as ethylene dichloride, or as any mixture thereof with each other and/or HCl . As will be seen hereafter one process of the invention involves recycling a product stream of ethylene dichloride. As mentioned, at least 1 gram atom of chlorine per mole of ethane must be utilized with the amount of chlorine generally ranging between 1 and 7.5 gram atoms of chlorine per mole of ethane, and preferably 1.5 to 5 gram atoms of chlorine per mole of ethane.

When describing the ratios discussed hereinbefore, the chlorine is chlorine which is considered to be available for the oxychlorination reaction. All of the chlorine from HCl and Cl_2 is, of course, available but only one atom per molecule is considered to be available from introduced ethylene dichloride. As used in the claims, the term "available chlorine" includes only one atom of chlorine per molecule of ethylene dichloride.

The oxygen is conveniently added in the form of air though more concentrated elemental oxygen may be used and should generally be present in amount of from 0.5 to 6 moles of oxygen per mole of ethane,

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though as mentioned, it is important that the upper limit of amount of oxygen be controlled in relationship to the amount of chlorine, so that the ratio of oxygen to available chlorine defined above is not exceeded.

As catalysts operative in the process of the invention there can be mentioned particularly the inorganic oxygen-containing compounds of multivalent metals. Included among such compounds are not only simple oxides but also oxychlorides. The catalysts can be initially introduced in the form of oxygen-containing compounds, such as carbonates, nitrates, phosphates and hydroxides, and thus inorganic compounds resulting from this form of introduction may also be present in the reaction zone. Thus, for example, metal phosphates may be present in the reaction zone when the catalyst is charged, for example as iron phosphate. As used in the claims a "multivalent metal oxide" not only includes simple oxides and oxychlorides, but more complex inorganic oxygen containing compounds including those which may be formed *in situ*, as for example from such inorganic compounds containing combined oxygen.

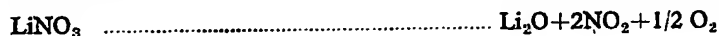
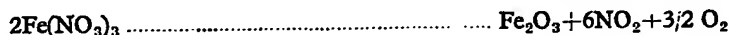
A large group of such multivalent metals suitable for making the catalysts useful in accordance with the invention include multivalent metals selected from Groups IVB, VB, VIB, VIIB, VIII, IVA, VA, and VIA, and the lanthanide series. As examples of such multivalent metals there may be espe-

cially mentioned, iron, cerium, manganese, uranium, vanadium, nickel, chromium and cobalt or any combinations thereof.

To the multivalent oxide catalyst components mentioned above there can be added promoters, such as inorganic compounds of Li, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Zn, Cd, B, In, P and Tl.

The oxidation catalyst is one of the known oxidation catalysts, for example one of those which are formed from a multivalent metal. It now appears that the most suitable such oxidation catalysts probably exist in the reaction zone in a form in which both oxygen and chlorine are bound.

Catalysts and notably the multivalent metal oxides are often used on a carrier as for example, aluminium oxide, silicon carbide, quartz, Vycor (Registered Trade Mark), pumice, silica gel or mullite. The catalyst may also be prepared unsupported by the use of pelleting techniques. The oxides forming the catalyst may be deposited on the carrier from a soluble salt, such as a nitrate of the element in question as for example, ferric nitrate and lithium nitrate may be added to water and the catalyst support is immersed in the aqueous mixture which is brought to its boiling point. Heating is continued until the nitrates are decomposed and the water is evaporated. An overall reaction for the decomposition may be written:



During this process the catalysts are deposited on the carrier which is then ready for use such as in a fixed bed reactor. Other forms of catalysts and methods of contacting the reactants therewith can be employed, such as fluidized bed techniques, using a finely divided catalyst or a gravity-flowing bed of catalyst particles. The contact time between the reactants and the catalyst under the reaction conditions may vary from 0.1 to 10 seconds. In some instances at least one of the catalyst components may be in a molten state, such as when an appreciable amount of lithium chloride is employed at the higher reaction temperatures.

The promoter compounds, such as the oxides, can be added in well known manner, as for example by adding a soluble salt which is decomposed and converted to the oxide, as indicated above. Other techniques, such as impregnation, may also be used. The relative weight ratio between the promoter and the multivalent oxide component may vary within extremely wide limits and amounts as low as 1% by weight have been found effective. Alternatively, the promoters may

constitute the predominant weight portion of the catalyst.

A preferred catalyst in accordance with the invention is iron oxide which may be used *per se* as the multivalent metal oxide, or which may be used in combination with other multivalent metal oxides or compounds. The iron oxide is advantageously promoted with a promoter as set forth above and especially lithium oxide or lithium chloride.

Cerium and manganese metal oxides may also be mentioned as good oxidation catalysts.

While it has been proposed to utilize steam as a coolant and/or diluent, in certain dehydrogenation reactions the use of water in accordance with our process in the amounts specified serves as an active and essential component controlling the reaction. It is believed that among other things the water controls the amount of metal chloride which may form on the catalyst surface thus maintaining a long catalyst life and controlling the catalyst activity so as to favour the desired dual reaction. The preferred amount of added water ranges between 2 and 20

moles per mole of ethane.

The water is, of course, converted to steam during the reaction and may be initially introduced in liquid, solid or vapour form.

5 It has been found that the use of the added water in amount specified herein enables one to charge any of the catalysts, if desired, in the form of a volatile chloride, such as FeCl_3 , because it has been found that the
10 water in such amount in the reaction zone converts the FeCl_3 to an at-least partially oxidized state which is not readily volatile. More important, in contrast to prior art processes, the use of water in the amount specified prevents the conversion of the oxidation
15 catalysts, such as the iron oxide, to a volatile chloride which is rapidly lost from the reaction zone.

20 The reaction may be effected at normal, sub-atmospheric or super-atmospheric pressure as, for example, pressures ranging up to 400 pounds per square inch absolute, though pressures between 50 and 250 pounds per square inch absolute are advantageous.

25 The hydrogen chloride, chlorine or mixture thereof is preferably added with the reactant feed, as is the oxygen-containing gas. If desired a portion of this gas i.e. chlorine-containing gas and/or the oxygen-containing gas may be injected into the reactor at a position downstream from the point
30 of introduction of the ethane feed. Similarly, the ethane feed may be split into several streams.

35 In addition to vinyl chloride, ethylene is produced as a product. This ethylene may be separated as a high purity material which is suitable for polymer production or for other requirements.

40 In addition to the vinyl chloride and ethylene, ethyl chloride, methyl chloride, acetylene and carbon oxides may be produced as by-products. The ethyl chloride may be suitably recycled to the process and the
45 acetylene may be selectively hydrogenated to ethylene in order to improve the overall yield of ethylene, or may be removed, for example, by absorption with cuprous ammonium hydroxide.

50 If it is desired to increase the yield of ethyl chloride with respect to the vinyl chloride yield, this may be achieved by a lowering of the temperature and in general a temperature about 50 to 100°C below the
55 optimum vinyl chloride operating temperature will increase the ethyl chloride yield.

As mentioned, the ethyl chloride may be recycled to the process for conversion to vinyl chloride and the main portion of the reactor feed may constitute ethyl chloride.
60 When using higher quantities of ethyl chloride in the feed, in general a slightly lower reaction temperature should be used than when utilizing ethane alone.

65 In accordance with a further embodiment

of the invention, the ethylene produced in the reaction after separation from the vinyl chloride may be converted to ethyl chloride or ethylene dichloride and recycled to the process in order to increase the vinyl chloride
70 yield. In accordance with one mode of operation the product stream from the reactor is treated in an absorber with a suitable solvent for the recovery of chlorinated hydrocarbons and the residual gas containing dilute ethylene is oxychlorinated to yield ethylene dichloride which is separated by distillation and recycled.

75 More specifically the reactor stream is cooled and water and hydrogen chloride removed by condensation. Residual hydrogen chloride and carbon dioxide are removed by scrubbing with alkaline solutions such as ethanalamines, NH_3 or carbonates. Then the reactor gas is compressed and scrubbed for removal of chlorinated hydrocarbons. Dichloroethylene, trichloroethylene, tetrachloroethane and other solvents are suitable.
80 Absorption at about 50-100 psi and near 0°C are suitable conditions for vinyl chloride removal. The solvent is then pumped to a stripping tower where the chlorinated products are recovered by heating the solvent. The stripped solvent is cooled and recycled to the absorber. The chlorinated products are separated and purified in a series of distillation towers. In the first tower ethyl chloride bottoms suitable for recycle to the main reactor are produced. Mixed overhead of vinyl chloride and methyl chloride is separated in the second tower. Vinyl chloride bottoms are produced, suitable for addition purification, inhibition and storage.

85 The ethylene-containing stream which leaves the chlorinated hydrocarbon scrubber is reacted to yield ethylene dichloride. When chlorine is available, this reaction is conveniently conducted at 25-40°C in a liquid solvent such as ethylene dichloride with FeCl_3 catalyst. Alternately, the chlorination may be conducted in the vapour phase at 100-200°C.
100 using a variety of catalysts including Fe_2O_3 .

In the absence of chlorine, hydrogen chloride may be reacted in the presence of oxygen with the ethylene stream over an oxychlorination catalyst, such as copper chloride or potassium chloride to yield ethylene dichloride. Temperature from 250 to 450°C. may be used. Fixed and fluid bed reactors are suitable. When oxychlorination is practiced, residual traces of hydrogen chloride are removed by washing.

105 The crude ethylene dichloride is readily condensed and separated from the diluents (nitrogen, traces of methane, etc.). It is purified by distillation and may be recycled to the main reactor with ethane feed, hydrogen chloride (or chlorine), water, oxygen-containing gas and any recycle ethyl chloride. In the reactor at 500 to about 675°C., ethane
125 130

is converted to vinyl chloride and ethylene, and ethylene dichloride is pyrolyzed to vinyl chloride and hydrogen chloride. This hydrogen chloride conveniently serves as a source of chlorine for the catalytic reaction of ethane to vinyl chloride.

The ratio of ethane to recycle ethylene dichloride may vary over a very wide range. Thus as little as 1 mole of ethane for every 10 moles of recycle ethylene dichloride may be fed to the main reactor. As much as 10 or more moles of ethane may be fed for each mole of recycle ethylene dichloride. Alternately, if an ethylene dichloride pyrolysis unit is available, the ethylene dichloride may be pyrolyzed separately and the hydrogen chloride may be recycled to the main reactor. However, it is advantageous to conduct the pyrolysis in the main reactor to avoid the need for recycling the hydrogen chloride separately. An added advantage is that the pyrolysis reaction of ethylene dichloride is endothermic and consequently a reduction in the overall exothermic nature of the reaction is effected.

In accordance with another mode of operation the product stream from the reactor may be treated to remove residual HCl, the vinyl chloride and other chlorinated hydrocarbons are removed by absorption utilizing a suitable solvent and the residual ethylene-containing gas is treated for water removal. Hydrogen chloride is then added to bring the hydrogen chloride:ethylene ratio near 1, and the ethylene is hydrochlorinated to ethyl chloride, the ethyl chloride recovered and recycled to the process.

More specifically the condensation of water and hydrogen chloride, the removal of carbon dioxide and the recovery and purification of chlorinated products may be effected in the manner described above in connection thereof with the conversion of ethylene to ethylene dichloride and the recycling.

The ethylene-containing stream from the stripper is dried and compressed with a slight excess of hydrogen chloride to about 75-300 psi and reacted over one or more of a variety of catalysts at 100-250°C. to yield ethyl chloride. Among the catalysts which are useful are zinc and copper chlorides, zinc chloride on charcoal, ferric chloride impregnated supports as well as a variety of other catalysts. With some classes of catalysts complete drying of the reactor feed gases is to be avoided. 10-20% moisture in the feed enhances the stability of these catalysts.

Ethyl chloride is recovered from the reactor product; it is freed of light boilers and purified in a train of distillation columns. Purified ethyl chloride is pumped to the main reactor and introduced with make-up ethane. It is also feasible to conduct the main reaction, conversion of ethane, as well

as ethyl chloride, to vinyl chloride, under pressure, up to 400 psi.

It is also possible to cool the product stream from the reaction in accordance with the invention and to pass the same into a chlorination reactor where chlorine is selectively added to the ethylene with little chlorination of vinyl chloride occurring. Chlorine adds to ethylene in high yields over catalysts such as iron or copper-containing catalysts, producing ethylene dichloride which may be readily pyrolyzed to yield vinyl chloride. The ethylene dichloride produced by the chlorination reaction of the ethylene may be readily separated from the gas mixture due to its high boiling point and serves as a source of both vinyl chloride and hydrogen chloride in the main reactor to which it may be recycled.

In any even, where the dichlorinated product is recycled this may be utilized as at least a partial source of the hydrogen chloride for the main reaction in accordance with the invention.

The following Examples are given by way of illustration.

EXAMPLE 1

Aluminium oxide (Alundum—Registered Trade Mark) pellets (1/8") were soaked in concentrated hydrochloric acid overnight, then washed with distilled water and dried at 105°C. 49.5 g. cerium nitrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, with 1.84 g lithium hydroxide monohydrate were added to 100 ml distilled water in an 800 ml beaker. A charge of 115 g of acid-washed Alundum was added. The solution was heated and heating was continued to dryness with stirring. The Alundum pellets were light yellow coloured and contained 14.4% actives. Catalyst composition was calculated to be 98% CeO_2 -2% Li_2O .

The catalyst was charged in the form of a fixed bed to a height of 30 cm. in a reactor tube having a 25 mm diameter made of Silica glass (Corning Glass Works "Vycor"—Registered Trade Mark). The reactor tube was mounted in a combustion tube furnace (Hevi-Duty Electric Company). The furnace consists of several electrical heating elements mounted so as to surround a central tubular reactor. The temperature of the catalyst bed was measured by use of an axial thermowell and thermocouple which was connected to a Pyr-O-Vane Temperature Controller (Minneapolis-Honeywell Regulator Company). The controller served to reduce the heat input to the furnace whenever the control temperature was exceeded.

Feed gases were fed to the system from gas cylinders. Flow rates were measured by used of capillary flow meters. Ethane, CH_4 , air, and steam were passed through the tube at normal pressure. Flow rate of ethane was 0.25 mole/hr.

The axial hot spot temperature was maintained as indicated in Table 1 below and the mole ratio of hydrogen chloride, oxygen, ethane and steam were varied as indicated in Table 1.

Analysis of products was made in general by vapour phase chromatography, using several different columns to identify and determine the quantity of each product. Periodi-

cally, the tail gas was scrubbed to remove CO_2 and HCl and then subjected to solvent absorption to recover vinyl chloride and methyl chloride. These components were separated by distillation and the vinyl chloride was purified by treatment with solid caustic pellets.

The results obtained are indicated in Table 1.

TABLE 1

Temp.°C	Feed Mol Ratio				% C_2H_6 Conv.	% Selectivity**			
	HCl	O_2	C_2H_6	Steam		Vinyl Chloride	Ethylene	$\text{CO} + \text{CO}_2$	Ethyl Chloride
650	3	1	1	6.2	98.5	21.4	52.4	9.2	3.6
	3	2	1	2.5	98.5	26.1	43.4	10.1	5.9

*Conversion is moles of ethane converted to products per mole of ethane fed to reactor.

**Selectivity to product A is moles of ethane converted to product A per mole of ethane converted to products.

EXAMPLE 2

An iron oxide-lithium oxide catalyst (95% Fe_2O_3 -5% Li_2O) was prepared on Alundum using $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and LiNO_3 in a manner similar to that outlined in Example 1. The catalyst contained 12.7% actives and was rust red in colour. The catalyst had a

surface area of $2.6 \text{ m}^2/\text{gr}$.

This catalyst was evaluated in a manner similar to that described in Example 1 using air as the source of oxygen. Ethane feed rate was 0.25 mole/hr. Several performance values are tabulated below:

TABLE 2

Temp.°C	Feed Mol Ratio				% C_2H_6 Conv.	% Selectivity			
	HCl	O_2	C_2H_6	Steam		Vinyl Chloride	Ethylene	$\text{CO} + \text{CO}_2$	Ethyl-Chloride
600	3	1	1	6.2	91.1	18.2	30.7	9.3	34.8
650	2	2	1	2.5	99.9	32.9	47.6	6.9	4.3
	3	2	1	2.5	99.2	42.4	43.2	8.0	0.8

EXAMPLE 3

Using the catalyst of Example 2, oxygen

was used in place of air. Steam:ethane ratio was 10. Results at 650°C were as follows:

TABLE 3

Temp.°C	Feed Mol Ratio			% C_2H_6 Conv.	% Selectivity			
	HCl	O_2	C_2H_6		Vinyl Chloride	Ethylene	$\text{CO} + \text{CO}_2$	Ethyl Chloride
650	2	2	1	100	24.0	57.4	8.5	0.9
	3	2	1	100	32.3	48.8	8.6	0.9

EXAMPLE 4

5 Catalysts containing manganese oxide were prepared from manganous nitrate solution using 1/8" diameter Alundum particles. In one case, cadmium nitrate was added to the manganous solution before evaporation and coating of the catalyst particles. The black

catalyst particles contained 20% actives and were fired at 650°C in a muffle furnace before testing. These catalysts were evaluated using the equipment and techniques described in Example 1. Results are tabulated below:

10

TABLE 4

Catalyst	°C Temp.	Feed Mole Ratio				% C ₂ H ₆ Conv.	% Selectivity to	
		HCl	O ₂	C ₂ H ₆	H ₂ O		Vinyl Chloride	Ethylene
Mn ₂ O ₃ - Alundum	500	1	1	1	10	32.5	28.3	41.6
95% Mn ₂ O ₃ - 5% Cdo - Alundum	500	1	1	1	10	72.2	28.3	24.8

EXAMPLE 5

15 To demonstrate that ethyl chloride is suitable for recycling to the oxidative dehydrogenation process reactor, the following experiment was conducted. Ethyl chloride was reacted in the presence of oxygen, hydrogen

chloride and steam (mole ratios relative to ethyl chloride were 1, 1, and 10, respectively). Ethyl chloride feed rate was 0.5 moles/hr. The experiment arrangement was as described in Example 1. Typical results were as follows:

20

25

TABLE 5

Catalyst	°C. Temp.	Feed Mole Ratio				% Vinyl Chloride	Yield
		HCl	O ₂	H ₂ O	EtCl		
CeO ₂ (97%)-Li ₂ O (3%) on Alundum	600	1	1	15	1	50.0	
10 Mn ₂ O ₃ .CeO ₂ on Alundum	600	1	1	10	1	41.0	
Mn ₂ O ₃ (97%)-Li ₂ O (3%)	600	1	1	10	1	38.9	
Fe ₂ O ₃ (95%)-Li ₂ O (5%)	650	2	2	10*	1	54	

*In this run ethyl chloride rate was 0.25 moles/hr.; air was the source of oxygen; the diluent was 7.5 moles N₂+2.5 mole H₂O.

EXAMPLE 6

The catalyst of Example 2 was evaluated in the manner described in Example 1. Air

was used as the source of oxygen. Several performance values are tabulated below:

30

TABLE 6

Temp. °C.	Feed Mole Ratio				% C ₂ H ₆ Conv.	% Selectivity	
	HCl	O ₂	C ₂ H ₆	H ₂ O+N ₂		Chloride	Chloride
550	1	1	1	10	67	62	2.1
600	2	1	1	10	81	30	14
	3	1	1	10	91	35	18

EXAMPLE 7

Aluminium oxide (Alundum) pellets (1/8") were soaked in concentrated hydrochloric acid overnight, then washed with distilled water and dried at 105°C. 48.4 g cerium nitrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), with 1.40 g lithium hydroxide ($\text{LiOH} \cdot \text{H}_2\text{O}$) were added to 100 ml distilled water in an 800 ml beaker. A charge of 115 g of acid washed Alundum was added. The solution was heated. Heating was continued to dryness with stirring. The Alundum pellets were light yellow coloured and were found to contain 19.6% actives.

Ethyl chloride was reacted in the presence of oxygen, hydrogen chloride and steam (mole ratios relative to ethyl chloride were 1, 1, and 10 respectively) in the arrangement described in Example 1 at a temperature of 550°C, using the catalyst described above. Conversion and selectivity values were 89 and 46% (vinyl chloride), respectively.

EXAMPLE 8

Using a Fe_2O_3 - Li_2O catalyst prepared as

noted in Example 2, the oxidative dehydrogenation of ethane was conducted in a manner similarly to that described in Example 1. Instead of hydrogen chloride, chlorine was used. Feed mol ratios for chlorine-oxygen-ethane-nitrogen plus steam were 1.5-2-1-10, respectively. At a temperature of 600°C, 100% conversion of ethane resulted with a 33% selectivity value to vinyl chloride. Selectivity to ethylene was 32.6%.

EXAMPLE 9

Using a 22 actives catalyst of composition $\text{Fe}_2\text{O}_3(95\%)$ - $\text{Li}_2\text{O}(5\%)$ prepared in a manner similar to that detailed in Example 2, and having a surface area of 3.7 m^2/gr , ethane was converted to vinyl chloride at 650°C using a feed of ethane- HCl - O_2 - N_2 + H_2O (mole feed ratios of 1-3-2-10). Air feed in one instance was introduced with the other components at the entrance of the reactor; in the second situation, half of the air was injected into the bed at the mid depth. Results were as follows:

TABLE 7

Air Feed	% C_2H_6 Conv.	% Selectivity			
		Vinyl Chloride	EtCl	$\text{CO} + \text{CO}_2$	Ethylene
Normal	100	38.0	3.5	21.8	31.7
Split	100	44.3	0.5	19.8	30.5

EXAMPLE 10

A catalyst containing 14% Fe_2O_3 was prepared by the evaporation of a $\text{Fe}(\text{NO}_3)_3$ solution with 1/8" diameter Alundum. The catalyst had a surface area 8.9 m^2/gr .

This catalyst was used in an attempt to

convert ethane to vinyl chloride in the reactor of Example 1. At 650°C, using mole feed ratios of HCl - O_2 - N_2 -ethane of 5-3-11.4-1 respectively, with 0, 3 or 7.6 moles of steam the following results were obtained:

TABLE 8

$\text{H}_2\text{O}/\text{C}_2\text{H}_6$ Level	% C_2H_6 Conv.	% Selectivity			
		Vinyl Chloride	EtCl	$\text{CO} + \text{CO}_2$	Ethylene
0		Operation was not stable without steam			
3	98.4	43.7	4.8	6.8	42.8
7.6	100	48.2	9.3	11.1	26.2

In the run without the steam, the operation was unstable since iron chloride continually formed and migrated through and from the reaction zone. This effect was prevented in the runs with added steam. While the several

beneficial effects of added steam are not all understood, it is believed that it also aids in keeping the catalyst free from coke, and that it keeps the iron in a more oxidized state. It will be noted that the run with 7.6

moles of steam gave a higher yield or selectivity of vinyl chloride, as well as a slightly higher conversion.

EXAMPLE 11

5 The conversion of ethane to vinyl chloride with ethylene recycle as ethylene dichloride was effected in a continuous operation. The main reactor was 8 feet long and fabricated of ceramic coated Inconel (Registered Trade Mark) tubing. It was mounted in an array of 4 combustion tube furnaces. The catalyst charge for this reactor was 14% actives of iron oxide-lithium oxide. The reactor bed temperature was monitored by use of an axial thermocouple.

15 The mole feed ratios to this reactor were ethane-hydrogen chloride-oxygen-steam = 1-2.3-1-6. Recycle ethylene dichloride was fed to the reactor at a position below the top of the catalyst charge. Maximum bed temperature was 620-630°C.

20 The product stream from the main reactor was quenched, water washed and caustic scrubbed. Vinyl chloride and a trace of ethyl chloride were recovered by absorption in dichloroethylene at 65 psia and -14°C.

25 The recycle ethylene stream was chlorinated to ethylene dichloride at an average temperature of 38°C at 58 psi using FeCl₃ dissolved in ethylene dichloride. Product was washed and then purified by distillation and recycled to the main reactor.

30 Over a 22-hour test period, an 81% (average) yield of vinyl chloride from ethane was measured.

EXAMPLE 12

35 The main reactor of Example 11 was used in an ethylene recycle process. Vinyl chloride recovery was based on the same absorption system. Feed ratios to the reactor were ethane-hydrogen chloride-oxygen-steam of 1-2.4-1-8.

40 The ethylene-containing gas was dried with calcium sulphate; dry hydrogen chloride was metered into this stream in 12% molar excess. The gas mixture was compressed to 230 psia and fed to a jacketed stainless steel reactor containing a catalyst of copper chloride promoted with zinc chloride on an alumina support. The temperature in the reactor was maintained by condensing dichlorobenzene at 185°C. The pressure of the product stream was reduced; residual hydrochloric acid was removed by water washing.

55 The ethyl chloride was condensed and recycled to the main reactor. An average vinyl chloride yield of 78% from ethane was determined in a 34-hour run.

EXAMPLE 13

60 Uranyl nitrate, UO₂(NO₃)₂·6H₂O was decomposed thermally from the melt which

contained 1/8" diameter silicon carbide pellets. The catalyst was heated to 475°C before being cooled. Gravimetric measurements indicated that the catalyst contained 17.3% actives.

EXAMPLE 14

A vanadium oxide catalyst was prepared by evaporating a suspension of vanadium pentoxide on α-alumina, 1/8" diameter.

EXAMPLE 15

A chromia-magnesia catalyst was prepared from a chromium nitrate and magnesium oxide slurry and 1/8" diameter α-alumina particle (specific surface 9.2 m²/g). The slurry was evaporated to dryness while the catalyst particles were continuously stirred. The dried catalyst was heat treated at 700°C for 18 hours before use. It analyzed 9.1% actives of a composition 82% Cr₂O₃-18% MgO.

EXAMPLE 16

Two catalysts were prepared using aqueous solutions with a ratio of M₂O₃:Li₂O of 95:5. An Alundum support was used. M was Co or Ni.

The catalysts of Examples 13-16 may be used to convert ethane to vinyl chloride in the manner described in Example 1.

WHAT WE CLAIM IS:—

1. A process for the catalytic conversion of ethane to vinyl chloride which comprises reacting a mixture of ethane, available chlorine and oxygen at a temperature between 500 and 750°C. in the presence of added water and an oxidation catalyst, said available chlorine being added in amount of at least one gram atom per mole of ethane and per mole of oxygen and said water being added in amount of at least 2 moles per mole of ethane.

2. A process according to claim 1 in which said chlorine is added in the form of Cl₂, HCl, ethylene dichloride or mixtures thereof.

3. A process according to claim 1 or claim 2, in which said oxygen is added in the form of air.

4. A process according to any of the preceding claims in which the reaction is effected at a temperature between 550 and 675°C.

5. A process according to any of the preceding claims in which ethylene contained in the reaction product is chlorinated to ethylene dichloride and the ethylene dichloride recycled to said reaction of ethane with the available chlorine and oxygen.

6. A process according to any of claims 1 to 4 in which ethylene in the reaction product is hydrochlorinated ethyl chloride, which is recycled to the reaction of ethane with the available chlorine and oxygen.

7. A process according to any of the pre-

- ceeding claims in which ethyl chloride is added to the reaction of ethane with the available chlorine and oxygen.
- 5 8. A process according to any of the preceding claims in which said oxygen is added in amount of 0.5-6 moles of ethane.
9. A process according to any of the preceding claims in which said catalyst is promoted with inorganic compounds of Li, 10 Na, K, Rb, Cs, Mg, Ca, Sr, Ba, Zn, Cd, E, In, P or Ti.
10. A process according to any of claims 1 or 8 in which said catalyst is an oxide of iron, cerium, manganese, uranium, vanadium, 15 cobalt, chromium or nickel.
11. A process according to any of the preceding claims in which said catalyst is deposited on a carrier.
12. A process according to claim 11 in which said carrier is an aluminium oxide 20 carrier.
13. A process according to any of the preceding claims in which said catalyst is promoted with lithium oxide.
14. A process according to any of the 25 preceding claims for the catalytic conversion of ethane to vinyl chloride substantially as herein described with reference to the Examples.
15. Vinyl chloride produced by the process 30 of any of the preceding claims.
16. Ethylene produced by the process of any of claims 1 to 4 or 6 to 14.

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